

# ENGINEERED FILM SURFACES VIA SPONTANEOUS PHASE SEGREGATION

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## ABSTRACT

A series of hyperbranched materials have been developed that allow for the transportation of desired functional groups to the surface of a polymer blend by simple solution casting techniques. These materials have been employed to transport polyoxometalates, or POMs, to the surface of a polyurethane-polyether copolymer film, providing for a 10x increase in POM concentration at the surface compared to the bulk. The films were evaluated using x-ray photoelectron spectroscopy (XPS) and contact angle analysis, and their surface chemistry was dominated by the hyperbranched polymer incorporated into the blend.

## 1. INTRODUCTION

The proliferation and availability of chemical warfare agents (CWA's) suggests that they will remain a serious threat to both ground troops and the populace at large for the foreseeable future. Steps must therefore be taken to reduce susceptibility to such attacks. Existing defenses employ bulky barrier suits for protection and aggressive cleaning solutions, such as DS2, for remediation. A more desirable approach is to develop materials that have the potential for autonomous decontamination which would reduce or eliminate the persistent threat posed by CWA's. One alternative to the existing technology employs high surface area membranes, acting as advanced filtration devices or providing a mechanism for permeability control. These physical performance characteristics may be enhanced through the development and integration of multifunctional materials that also perform catalytic decontamination or detection.

Incorporating functional sites into a polymer surface provides these properties, but bulk incorporation techniques can be detrimental to the properties of the resultant material and are inefficient methods of surface

modification. Developing self-segregating additives for the transport of catalytic sites to a surface interface reduces impact upon bulk physical properties while maximizing the amount of material at the surface available for response to environmental changes. Hyperbranched polymers (HBPs) provide an ideal scaffold for the preparation of such multifunctional materials. A library of end group modified HBP was prepared, and their performance as surface modifiers was evaluated. Selected HBPs were then used to transport catalytic sites to a substrate surface.

## 2. EXPERIMENTAL DETAILS

### 2.1 Materials

Common chemicals were obtained from Alfa Aesar or Aldrich and were used as received. Polyethyleneimine (PEI) was obtained from BASF Corp. Methacrylate-functionalized fluorosurfactant was obtained from DuPont. Aliphatic epoxies were provided by Resolution Performance Products. Noveon provided thermoplastic polyurethane (TPU) as the bulk matrix for these experiments.

### 2.2 Chemistry

A representative procedure is given for the preparation of PEI HBP functionalized with perfluorinated and aliphatic chains. To a 40 mL screw top vial was charged hyperbranched polyethyleneimine (PEI, 3.08 g) followed by methacrylated fluorosurfactant (1.59 g). The two fluids were mixed vigorously to provide a homogenized suspension. The vial was then placed in a multi-well reactor at 65 °C for approximately 1.5 h, with periodic agitation to maintain the suspension. Then an aliphatic epoxy (2.57 g) was added to the vial and the mixture was periodically agitated. After heating for an additional 2.5 h, the vial was removed from the heating block and placed in a refrigerator. The polymer

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formed off-white viscous oil. The polymer was analyzed and used without further purification. Examination with FT-IR techniques confirmed full reaction of the methacrylate and epoxy. The carbonyl was observed to shift from 1728  $\text{cm}^{-1}$  to 1738  $\text{cm}^{-1}$  upon consumption of the methacrylate group. The epoxy band at 915  $\text{cm}^{-1}$  was also consumed over the course of the reaction.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 3.60-3.30 (5 H, from aliphatic additive), 2.71, 2.64, 2.58, 2.50, 2.46 (contribution from  $-\text{CH}_2\text{CH}_2\text{NH}-$  backbone, 27 H), 1.48 (2 H), 1.18 (16 H), 0.80 (3 H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 71.6, 71.5, 54.3, 54.2, 52.9, 52.3, 49.2, 47.4, 41.5, 39.7, 31.7, 29.5, 29.2, 26.0, 22.5, 14.0, 13.9( $-\text{CH}_3$ ).

### 2.3 Film Preparation

Prior to film formulation, stock solutions of both the matrix polymer and additive (HBP) were prepared at concentrations of ca. 30 mg/mL. Tetrahydrofuran (THF) was used to solvate the mixed end group PEI, though mixtures of THF-MeOH or another very polar solvent were required to solvate the HBPs functionalized with only perfluorinated chains. The appropriate volumes of stock solutions were then combined to give the desired relative concentration of bulk polymer to additive. The prepared homogeneous solution of bulk polymer and additive was cast onto a glass slide covered with a Petri dish lid. This provided a solvent-saturated atmosphere to slow evaporation and reduced the occurrence of drying defects during film formation. After drying ca. 16 h, the films were examined using contact angle analysis and XPS analysis.

### 2.4 Analytical Procedures

Infrared spectroscopy was performed using a Spectrum 2000 FT-IR spectrometer from Perkin-Elmer. Films were cast on 25 mm NaCl plates from THF, and recorded under absorbance mode (64 scans, 2  $\text{cm}^{-1}$  resolution). Nuclear magnetic resonance spectroscopy was carried out using a Bruker-Biospin 600 MHz Ultrashield Avance spectrometer, equipped with a standard bore broadband probe (5 mm OD tubes, 32 scans, 5 sec d1). Spectra were obtained in  $\text{CDCl}_3$  at room temperature, and all resonances are reported as ppm referenced to the residual solvent peak ( $\delta$  7.26 ppm).

Contact angles were recorded using a goniometer equipped with a CCD camera and an image capture program employing LabView software. Contact angles were measured using HPLC grade water by defining a circle about the drop, and recording the tangent angle formed at the substrate surface.

Near surface compositional depth profiling was performed using the Kratos Axis 165 X-ray photoelectron spectroscopy system, equipped with a hemispherical

analyzer. A 100 W monochromatic Al Ka (1486.7 eV) beam irradiated a 1 mm x 0.5 mm sampling area. Angle resolved X-ray photoelectron spectroscopy (AR-XPS) was utilized with data acquired at 30° and 90° take off angle (TOA). Shallow TOAs accentuate the spectral contributions of any component that has segregated to the surface. Survey scans were taken at pass energy = 80 eV. Elemental high resolution scans for C1s, O1s, N1s, and F1s were taken at pass energy = 20 eV. Kratos' VISION 2 software was utilized for all data analysis; linear background subtraction, curve fitting, peak integration, and charge compensation.

## 3. RESULTS & DISCUSSION

### 3.1 Synthesis

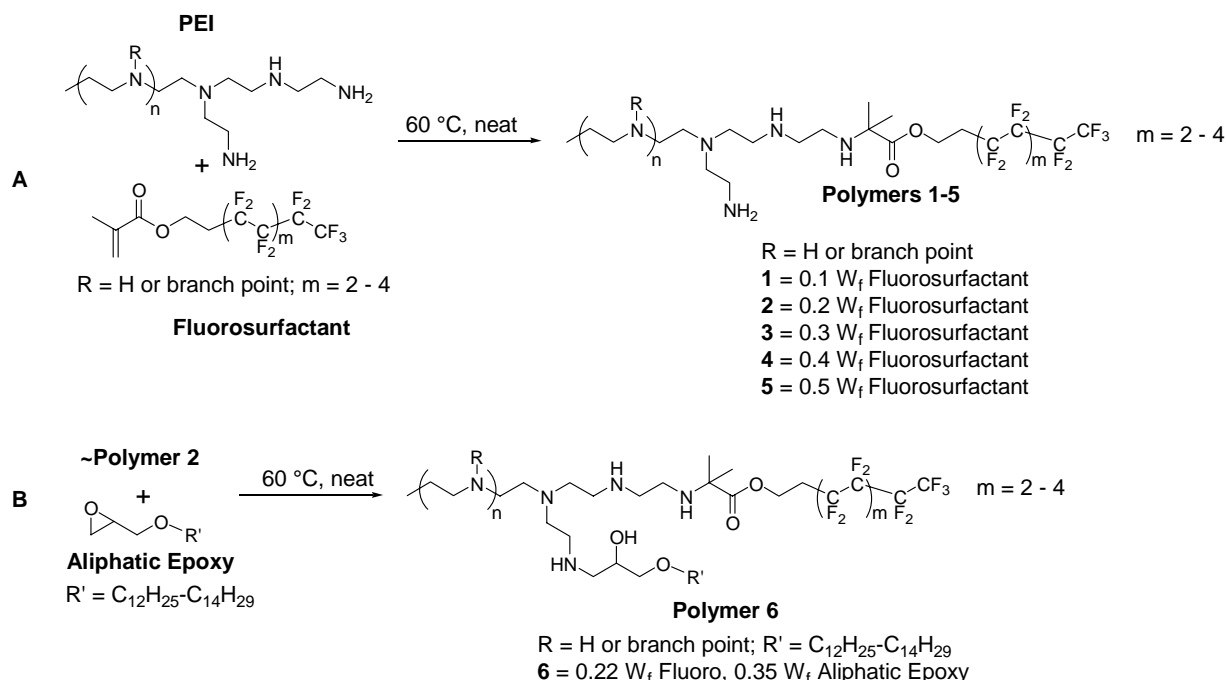
The route employed for the modification of hyperbranched polyethyleneimines (PEIs) is shown as Scheme 1. The fluorosurfactants were added via Michael addition to the amine termini of the polymer. The shift in carbonyl absorbance of the fluorosurfactant was tracked using FT-IR, changing from 1728 to 1739  $\text{cm}^{-1}$  upon the consumption of the methacrylate group. The reaction required ca. 3 h to reach completion at 60 °C. Polymers **1-5** contained only the fluorosurfactant as an additive (10 wt% for **1**, 20 wt% for **2**, etc).

**Table 1: Composition of Modified HBPs**

Polymer	1	2	3	4	5	6
W <sub>F</sub> Fluoro	0.1	0.2	0.3	0.4	0.5	0.22
Mol <sub>F</sub> Fluoro	0.023	0.052	0.089	0.139	0.208	0.10
W <sub>F</sub> Alkyl	-	-	-	-	-	0.35
Mol <sub>F</sub> Alkyl	-	-	-	-	-	0.45

**Note:** W<sub>F</sub> indicates weight fraction perfluorinated chains. Mol<sub>F</sub> indicates mole fraction relative to 1° amine end groups. The base polyethyleneimine has a ratio of 1°: 2°: 3° amines of 1.0: 0.91: 0.64

Polymer **6** contained ca. 22 wt% perfluorinated chains but was also reacted with an aliphatic epoxy, which was added to the reaction mixture after the methacrylate of the fluorosurfactant had fully reacted. After an additional 2.5 h the reaction mixture was cooled. The modified HBP products were used without further purification. Examination of polymer **6** by  $^1\text{H}$  NMR confirmed the consumption of the epoxy (coalescence of well-defined resonances confirmed ring-opening) group. Analysis with FT-IR also indicated the disappearance of the characteristic epoxy absorption at 915  $\text{cm}^{-1}$ , and the  $-\text{OH}$  peak resulting from the epoxy ring-opening intensified and broadened the amine peaks arising from the polymer backbone. The resulting polymers (**1-5**) had limited solubility in common organic solvents (e.g. THF,



**Scheme 1: Methods of PEI Modification**

Route A: Neat Michael addition of methacrylate to amine end groups

Route B: Epoxy ring-opening by amine end groups

CH<sub>2</sub>Cl<sub>2</sub>), which decreased as the fluorine content increased. Polymer **6** was therefore functionalized with aliphatic chains to improve solubility in common organic solvents. Solubility remained good for all polymers in binary solutions of THF and water or methanol. Compositional data for the polymers is presented in Table 1.

### 3.2 HBP Polymer Blend Cast Films

The segregation of the modified HBPs was evaluated using a commercially available system. The HBP backbone was maintained constant (e.g. molecular weight, branching) for each polymer prepared. By varying the average degree of functionalization the thermodynamic driving force for segregation could be varied. Several polymers were considered as matrix materials, but the candidate chosen for modification was a thermoplastic polyurethane (TPU). The TPU chosen was a polyurethane-polyether copolymer with large segments of polyethylene oxide in the polymer backbone. Solutions of TPU and HBP were prepared so that they contained 1 % by mass fluorosurfactant. Control samples were also prepared, containing only TPU and either the unreacted fluorosurfactant or unmodified PEI. Therefore all of the samples (except the TPU and PEI-TPU controls) contained the same bulk concentration of perfluorinated components. The solutions were then cast onto silicon substrates and dried slowly.

The primary tool for the HBP evaluation was intended to be XPS analysis, though contact angle analysis proved to be a rapid method for surface property evaluation. Advancing and receding contact angles were determined for the blended films using HPLC-grade water. Figure 1a shows the behavior of cast films containing 1% wt/wt perfluorinated component. The contribution from the HBP backbone therefore varied, ranging from ca. 1.3% wt/wt for HBP **5** (high loading on the HBP core) to ca. 6.2% wt/wt for HBP **1** (lowest loading on HBP core). Figure 1b shows the behavior of the HBP additives when they were included at a constant level (1% wt/wt), regardless of level of end group modification. To provide context for the observations, TPU was also studied with unmodified PEI as an additive and small molecule fluorosurfactant as an additive. Both situations resulted in minimal changes in contact angle (~3°) indicating that separately neither additive impacted the film surface.

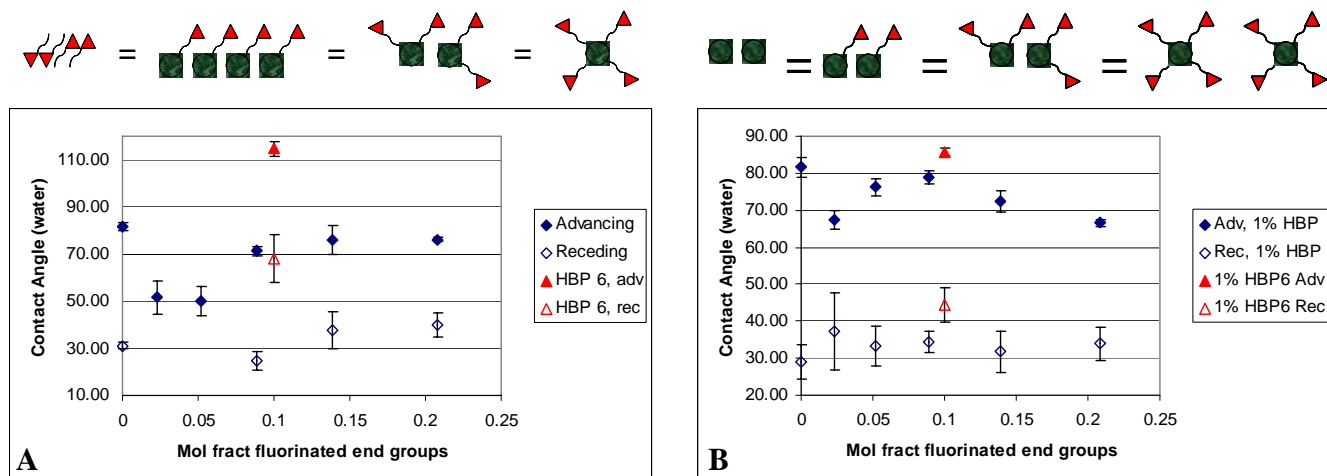
In contrast, when the perfluorinated component was bound covalently to the PEI backbone, significant changes in contact angle were observed. Both HBP's **1** and **2** exhibited a dramatic increase in hydrophilicity at the polymer surface. The receding contact angle is not reported for these samples because the angle was too low to be accurately measured (<10°). Samples with HBP **3**, **4**, and **5** exhibited a relative increase in hydrophobicity, approaching the behavior of the base TPU. Polymer **6**, with both aliphatic and perfluorinated end groups,

exhibited the highest hydrophobicity of the modified HBPs.

The trends observed in Figure 1 indicate that both the composition of the HBP and its concentration have a significant impact upon its performance as a surface modifying additive. The surface characteristics of the TPU were not modified significantly by the addition of either the base PEI polymer or the fluorosurfactant alone. The substrate surface energy was increased (effectively wetted by H<sub>2</sub>O) when the HBP contained low fluorine loading and was present in high concentration (HBP 1 & 2, 1% wt/wt fluorinated component). When the HBPs were modified with high levels of perfluorinated chain ends, the surface energy of the substrate was not significantly altered except for the case of polymer 6, where a majority of the end groups were consumed by perfluorinated and aliphatic chain ends. The fluorosurfactant component of the HBP was expected to reduce the surface energy of the blend, though only polymer 6 exhibited this behavior. The hydrophilicity of the modified HBPs was expected, due to the low mole fraction of the total chain ends modified by the Michael addition chemistry. Even when incorporated at 50% by mass, the mole fraction (Mol<sub>f</sub>) of reacted end groups was only 10%. If sufficient HBP was incorporated into the blend, then the hydrophilicity of the amine dominated surface interactions. When the water came into contact with the surface, the hydrophilicity of the amines dominated the interaction, leading to a reduction in observed contact angle. A similar switching effect has been reported for linear block copolymers, whereby hydrophilic blocks were masked from the environment until they come into contact with water vapor (Anastasiadis, et al., 2003). Perfluorinated chain ends have also been driven away from a surface by annealing in hydrophilic conditions (Tanaka, et al., 2003). Here, the

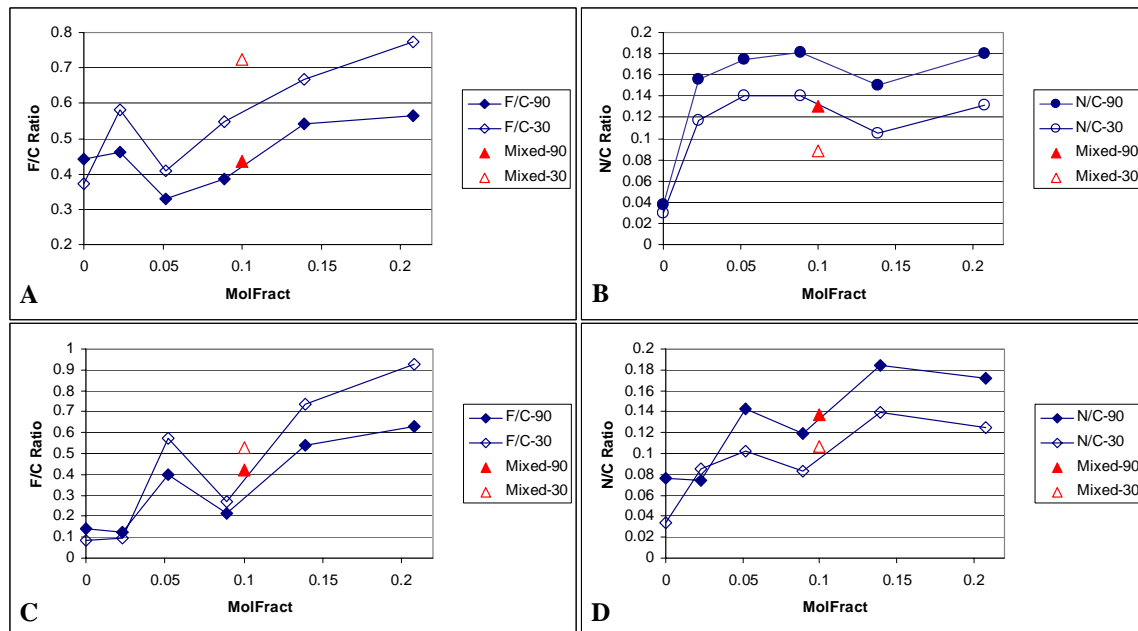
perfluorinated groups and amine backbones are intimately intermixed, and the response of the HBP to external stimuli is almost instantaneous. Only when a significant portion of the amine end groups were consumed (6) did the polymer exhibit the anticipated decrease in surface energy.

Angle resolved X-ray photoelectron spectroscopy (AR-XPS) was used to profile the composition of elements at the TPU blend film surfaces. Characteristic photoelectrons emitted from an element have a known attenuation length ( $\lambda_{AL}$ ) that determines the sampling depth ( $= 3\lambda_{AL}$ ). The TOA also influences sampling depth, such that  $depth = 3(\lambda_{AL})\cos(TOA)$ . Therefore shallow TOAs accentuate the spectral contributions of any component that has segregated to the surface. Data was acquired at 30° and 90° take off angles. Figures 2 and 3 show the atomic abundance of F and N relative to C, determined at take-off angles of 90° and 30°. The blends incorporating the modified HBPs exhibited noticeably higher nitrogen content at the film surface. A slight increase in nitrogen level was observed for the PEI sample with no perfluorinated groups, but the modified HBPs demonstrated higher surface nitrogen levels as well as the change in surface energy previously mentioned. Strong fluorine signals provided further evidence for phase segregation of the fluorinated HBPs at the surface. Observation of fluorine at a surface is a common technique to show the phase segregation of a polymer (Affrossman, et al., 1996; Sugiyama, et al., 2002; Hirao, et al., 2002). There is a clear trend for the elemental abundance of fluorine to increase as the angle of observation becomes shallower, indicating an increase in fluorine near the substrate surface. Perfluorinated chains have been shown to align perpendicular to a substrate surface as a polymer grafted side chain monolayer (Sun, et al., 1994) or as constituents of a Langmuir Blodgett thin



**Figure 1: Contact angles w/ H<sub>2</sub>O**

Contact angles determined from cast films of TPU with (right) 1% wt/wt perfluorinated component or (left) 1% wt/wt HBP additive. Error bars indicate one standard deviation from at least five measurements. Illustrations at top indicate (right) constant fluorosurfactant loading or (left) constant HBP loading.



**Figure 2: Relative atomic abundance of C, N at TPU-HBP film surface, determined via AR-XPS**

Plots show abundance of fluorine and nitrogen, normalized to the carbon signal for each sample. A&B plots show evaluation of 1% fluorine loading, C&D show evaluation of 1% additive loading. Elevated fluorine levels confirm the presence of perfluorinated chains, while elevated nitrogen levels for samples incorporating modified HBPs 1-6 indicates that the polymer backbone was also transported to the surface of the film (i.e. covalently attached to perfluorinated chains). Control samples (0 MolFr) points contained additives of 1% fluorosurfactant (A&B) or 1% PEI (C&D). Lines are provided only as guides for the eye.

film(Ha, et al., 2000). The orientation of perfluorinated polymer chain ends could cause the trends observed here, while the presence of both fluorine and elevated nitrogen levels at the surface confirms the migration of the HBPs.

Comparison of figures 1 and 2 is revealing as to the effect of additive loading of the systems. The influence on surface energy was revealed in figure 1, and it is clear that influence scales with total additive level. The trends for figure 2, though, suggest that the atomic compositions of the two films are nearly the same regardless of the initial loading level. This suggests that the HBP is segregating near the surface in sufficient quantity in both cases to generate a layer several nanometers in depth with similar elemental composition.

The increased presence of fluorine at the surface relative to the fluorosurfactant control sample indicates that the covalent attachment of the perfluorinated chains to the HBP either increased the net driving force for surface migration or increased the efficiency of the migration. The driving forces for the phase segregation result from both incompatibilities between the HBP and the polyurethane-polyether backbone of the matrix as well as the disparate surface energies of the constituent materials. Thermodynamics provides the driving force for the surface selective distribution of modified HBPs because they satisfy key enthalpic and entropic criteria.

From the Flory-Huggins expression for the free energy of mixing (Eq. 1) and the Young equation for surface free energy (Eq. 2), selective migration to the polymer/air interface requires an additive with a highly incompatible solubility parameter ( $\delta_2$ , driving the phase segregation) and a very low critical surface tension ( $\gamma_c$ , where  $\gamma_c = \gamma_{sl}$ , directing the phase segregation). Given the behavior of the PEI control sample, the hydrophilicity of the backbone coupled with the solubility parameter mismatch between the PEI and TPU backbones did not result in significant surface segregation of the HBP. Fluorinated additives fulfill both thermodynamic requirements discussed above, and a greater effect was observed when the perfluorinated groups were covalently attached to the HBP.

$$\Delta G_m = V_m(\partial_1 - \partial_2)^2 \phi_1 \phi_2 + RT(\chi_1 \ln \phi_1 + \chi_2 \ln \phi_2) \quad (1)$$

$$(\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta + \Pi_s) \quad (2)$$

Much published work has described the behavior of linear polymers with perfluorinated segments as pendant groups and chain ends, <sup>Error! Bookmark not defined.</sup> and as a function of molecular weight(Mason, et al., 2001). The perfluorinated segments have a greater effect upon surface chemistry when attached as chain ends. They have more mobility and increased free volume when compared to side chains of the main polymer, which

allows for surface enrichment in fluorinated segments. Unsurprisingly, their influence is also inversely proportional to the chain length of the parent polymer. The behavior of the modified HBPs makes sense when viewed in this context—the HBPs function as low molecular weight non-entangling polymer chains with a large number of chain ends, which promotes the surface segregation of the branched polymer. Partial fluoro-substitution of the chain ends is sufficient to drive the segregation and permits unreacted chain ends of the hyperbranched polymer to be modified as necessary (e.g. solubilizing groups, crosslinkable sites, etc.). The thermodynamically favored surface migration effectively “floats” the entire hyperbranched polymer to the surface of the polymeric matrix, delivering any attached reactive group to the surface.

The contact angle measurements observed in a thermoplastic matrix indicate a change in molecular order at the surface. Switching is achieved by molecular motion of the perfluorinated chains away from the surface upon contact and wetting by less-compatible (relative to air) solvents resulting in molecular “flipping” to the thermodynamically favored reactive functionality. The flip is instantaneous in a low  $T_g$  thermoplastic matrix. Given sufficient end group substitution and control over matrix selection, it may be possible to prepare a HBP that directs surface migration while protecting a labile reactive group. At the surface, the reactive group could then be exposed with environmental change acting as the trigger for presentation.

### 3.3 HBP-POM Hybrid Properties

The behavior of the modified HBPs indicates that a relatively low loading of perfluorinated and aliphatic chains are sufficient to carry the HBP to the surface. The remaining functionality on the PEIs presented an opportunity to expand the capabilities of the additive. The primary approach we investigated was the incorporation of polyoxometalates (POMs) into the HBP structure. The specific POMs of interest were Keggin-type oxoanions with molecular formulae of  $H_5PV_2Mo_{10}O_{40}$  ( $H_5POM$ ) and  $Na_5PV_2Mo_{10}O_{40}$  ( $Na_5POM$ ). These POMs have been shown to degrade chemical warfare agents (Boring, et al., 2001; Johnson et al., 1999), and the thermoplastic polyurethanes used as a bulk matrix may have applications in textile fibers. The resulting blend of POM hybridized with HBP in the TPU matrix may exhibit POM functionality at the surface (transported by the HBPs) to provide a self-decontaminating surface.

In the current system, the HBP was envisioned to interact with the POM as either a ligand for the molybdenum and vanadium or it would function as the counteraction by forming the ammonium salt with the

POM. Solutions of known concentration were prepared of HBP **6** and the indicated POM. Combining solutions of both polyoxometalate and HBP resulted in the immediate formation of a green precipitate that proved insoluble in all common solvents. The addition of a stoichiometric amount of acid (based upon the total amine content of the HBP backbone, including 1°, 2°, and 3° amines) disrupted the precipitate and enabled the formation of homogeneous solutions. The precipitates were dark green in color, which then dissolved to dark green solutions that then lightened to yellow several minutes after the addition of the acid. The initial POMs appeared reddish ( $H_5POM$ ) or orange ( $Na_5POM$ ). The color change indicated the formation of different charge transfer complexes with the metalates due to interaction with the polyamine.

This mechanism of interaction is supported by FT-IR analysis of the HBP-POM complex. Films of HBP, POM, and the HBP-POM complex were cast on salt plates and then subjected to infrared absorption spectroscopy. The native POMs exhibit different absorption maxima based upon their counteraction, with the protic species absorbing at ca.  $792\text{ cm}^{-1}$  and the sodium species absorbing at ca.  $784\text{ cm}^{-1}$ . Upon complexation with the protonated HBP, the complexes exhibited an absorption peak at ca.  $800\text{ cm}^{-1}$ , regardless of the initial counteraction. This collapse of the absorption peak indicates that the HBP has displaced the sodium or proton and is now acting as the counteraction for the POM.

**Table 2: IR Absorptions of POMs and HBP-POM Complexes**

$H_5POM$	$Na_5POM$	$6+H_5POM + HCl$	$6 + HCl + H_5POM$	$6 + Na_5POM + HCl$	$6 + HCl + Na_5POM$
792.5	783.9	801.9	802.9	799.1	799.0
870.8	862.7	870.2	870.9	868.3	867.8
958.4	948.2	952.8	953.2	949.5	948.4

The stability of the POM in the environment of the PEI backbone was also unknown. These POMs have been reported to be most stable at acidic pH, while the interior of the PEI is a basic environment. To determine if the environment of the HBP interior degraded the POM, cast films were again examined using FT-IR spectroscopy. To ascertain their stability, samples were prepared where the order of reagent addition was varied (e.g.  $POM+HBP$ , then  $HCl$  vs.  $HBP+HCl$ , then  $POM$ ). The spectra were found to be nearly identical regardless of the order of addition, suggesting that the POMs were stable to the HBP upon the formation of the green precipitate. Table I catalogs the prominent absorptions of the HBP-POM complexes, and the order of addition did not cause shifts for either POM. The consistency of the IR absorptions and their independence with respect to initial cation indicate the prominence of the ammonium salt as the determining interaction.

The behavior of the POM-HBP hybrids was then examined in the TPU matrix, employing both contact angle analysis and AR-XPS. A series of three compositions was prepared for both the sodium (IV-VI) and protic (I-III) metal oxides (see Table 3 for compositions). Relative to the TPU matrix, POM was incorporated 1 % by mass in the samples. Loading of HBP was 0.7 % (I and IV), 1.4 % (II and V), or 2.1 % (III and VI) relative to the TPU matrix mass. Stoichiometrically, the total amine content (1°, 2°, and 3°) of the HBP backbone was in excess in each sample. The low HBP content samples (I and IV) contained ca. 2.8 equiv amine/ammonium relative to the oxoanions of the POM, ranging up to ca. 8 equiv of amine/ammonium loading at the high end (III and VI). Table II also reports the advancing contact angle of water on the TPU and HBP-POM blend surface. The behavior of the HBP-POMs deviates from the trend observed using only HBP as an additive, where HBP 6 acted to increase the hydrophobicity of the surface of the TPU. Almost all of the samples exhibited an increase in surface energy. The most likely cause was the protonation of the PEI backbone to form the ammonium salt that exerted increased influence over the surface chemistry of the blend. The HBP polymer combined with acid (equivalent loading to II and V) in the absence of POM also exhibited an increase in surface energy.

**Table 3: Composition and Properties of HBP-POM Complexes**

Sample	TPU Equiv.	POM Identity	POM Equiv.	Prot. 6 Equiv.	Adv. Cont. Ang.	Std. Dev.
I	1.0	H <sub>5</sub> POM	0.010	0.007	89.3	6.6
II	1.0	H <sub>5</sub> POM	0.010	0.014	47.2	6.1
III	1.0	H <sub>5</sub> POM	0.010	0.021	22.4	3.6
IV	1.0	Na <sub>5</sub> POM	0.010	0.007	63.6	5.1
V	1.0	Na <sub>5</sub> POM	0.010	0.014	19.6	1.5
VI	1.0	Na <sub>5</sub> POM	0.010	0.021	23.9	1.6
6+H	1.0	-	0.000	0.014	16.6	0.4

While the contact angle data is useful for demonstrating that the HBP is still migrating to the surface of the film, the analysis can provide no data about the distribution of metal in the sample. For that information AR-XPS analysis was again used to interrogate the surface of the films (see Table 4). The fluorine concentration of samples doped with the hyperbranched additive increased as the take-off angle became shallower. A small amount of metal was also observed at the surface, primarily molybdenum with trace amounts of vanadium. These observations were consistent with the relative abundance of Mo and V for the POM, within experimental uncertainty. At 1% loading by weight, the expected elemental abundance of Mo was less than 0.2%. The observation of greater than 2% Mo, while still a small amount, indicates that the POM was transported to the surface effectively by the HBP. The appearance of increased oxygen, when compared to protonated HBP 6 in TPU (second row of

data, Table IV), is also indicative of efficient POM surface transport. The blend containing protonated HBP in TPU exhibited low oxygen content at the surface of the film (ca. 10%), whereas the films containing the protonated HBP-POM complex exhibited oxygen content near 20 %. For each molybdenum atom, the POMs contained four oxygen atoms, so the increase in observed oxygen is further evidence of POM presentation at the surface, and confirms the relative abundance of Mo as between 2% - 3%.

The films were prepared with a constant amount of POM relative to TPU concentration (ca. 1% by mass), so the amount of hyperbranched polymer additive increased in each sample in the series. Consequently, the proportion of fluorine present at the surface increased across each series, which is reflected in the observed elemental abundance. As the quantity of HBP additive increased, the amount of POM appeared to remain constant or decrease slightly. The drop in observed oxygen content was offset by increases in the fluorine content (due to the increase of HBP concentration), while the level of molybdenum remained constant within the error of the instrument.

**Table 4: AR-XPS Analysis of HBP-POM in TPU**

Polymer	90° TOA - Atomic Comp.				30° TOA - Atomic Comp.			
	C	F	Mo	O	C	F	Mo	O
POM + TPU	79.32	-	-	18.09	62.75	-	-	15.62
TPU + HBP 6-H <sup>+</sup>	64.28	13.52	-	9.59	68.23	12.90	-	7.84
I	61.61	10.31	2.90	24.02	60.54	17.48	2.34	18.33
II	61.65	14.51	2.31	19.11	60.25	22.18	1.99	13.30
III	62.11	16.56	1.73	16.26	60.14	23.56	1.54	11.62
IV	63.33	11.39	2.30	21.70	62.30	17.45	2.14	16.79
V	63.80	12.03	2.65	18.71	63.59	17.80	2.21	13.55
VI	63.61	13.49	2.10	19.09	58.66	24.10	1.94	13.68



The observation that the POM elemental concentration remained relatively constant suggests that the POM is saturating the available HBP, even at the highest level of HBP loading. This eventuality is not wholly unexpected, as the listed  $M_w$  for the base PEI was only 1300 Da. The polymer backbone is therefore relatively small and compact, and likely cannot accommodate more than one POM cluster per HBP. Further experiments with higher  $M_w$  PEIs have not been executed, but they may provide a more capable transport system for the presentation of POMs at a substrate surface. The current system, however, has produced an order of magnitude increase of POM at the film surface relative to the bulk loading of the film. Furthermore, when added to the polymer matrix without the HBP, the POM was not observed by XPS at the film surface. Covalently modified hyperbranched polymers may therefore act as transports for catalytic species to generate low cost additives that provide tailored polymer surfaces.

#### 4. CONCLUSIONS

We have demonstrated the ability of a hyperbranched polymer blended into a linear polymer matrix to migrate to an interface and transport other molecules or functional groups. In this way the HBP mitigates the distribution of other molecules in the matrix, and may provide a novel approach to the preparation of functional interfaces. Hyperbranched polyethyleneimines were functionalized with perfluorinated and aliphatic end groups and were then combined with polyoxometalates as counteranions. The resulting complex was soluble in organic solvents and could be combined with a thermoplastic polyurethane. The resulting films exhibited changes in surface energy and surface composition, which scaled with surface depth and quantity of HBP. Metal was observed at the film surface using AR-XPS, indicating that the POMs were transported to the surface successfully by the modified HBPs. Current research is focused on determining the influence of HBP molecular weight and determining the catalytic activity of the POM-HBP complexes transported to the surface.

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